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Specification

Title of the Invention :

Method of evaluating the structure of a material

Claims:

1. A method of evaluating the structure of a material in which the crystallinity of the material is measured by taking notice of one or more of spectral bands in the Raman scattering spectrum of the material and utilizing that the half width thereof or the scattering band intensity of a skirt portion of the spectral peak increases as the crystallinity of the material is worsened.

Detailed Description of the Invention

The present invention provides a method of evaluating the crystallinity, mainly, the grain size of polycrystal of Si or other materials and, in particular, it relates to a method which is particularly effective in a case where the structure

of the material varies or is present in a wide range including amorphous, polycrystal and single crystal structures.

For example, when an Si thin film is deposited on a quartz plate by heat decomposition of silane (SiH_4), it becomes amorphous upon deposition or heat treatment after the deposition at 600 °C or lower, and becomes polycrystal at 700 °C or higher. The situation can be observed by electron diffraction images but this is not simple and convenient because a specimen has to be placed in vacuum. In addition, in a case of the polycrystals, if the axes of microcrystal are aligned to some extent, spots appear in the diffraction images making quantitative evaluation difficult. In this regard, vacuum is not necessary in the use of Raman spectrometry and this can be used conveniently with no requirement of taking the crystal orientation in consideration since the Raman scattering includes no anisotropy when the crystal form is of a cubic system as in Si. In addition, when the Raman scattering attributable to impurities or lattice defects, there is also a possibility that impurities can be identified. As described above, structures of materials widely ranging from amorphous, polycrystal to single crystal can be evaluated simply and conveniently by using the method of the invention. Then, the Raman scattering is non-elastic light scattering caused by lattice vibrations in the material, and it is necessary to preserve the energy and the momentum before and after the

scattering. Fig. 1 schematically illustrates a dispersion relation of the lattice vibrations in crystals. Since the wave number q at the Brillouin zone end is about ~ 10^8 cm^{-1}, while the wave number k of light is about ~ $10^5 cm^{-1}$ considering a region near visible light, it can be seen that the lattice vibrations scattered in the course of the Raman scattering only consists of a mode $q \approx 0$ in the figure. Considering the Raman scattering process, scattered light appears on a lower energy side and a higher energy side of an incident light energy corresponding to emission and absorption of lattice vibrations in the vicinity: $q \approx 0$ as shown in Fig. 2. They are usually referred to as stokes line and anti-stokes line respectively. The difference between the wave number of the scattered light and the wave number of the incident light is $\pm\Delta k$. Relative to Δk, the Raman spectrum usually shows the scattering band intensity thereof.

Raman scattering in a polycrystal is to be considered. As the grain size becomes smaller (assuming grain size as D), it results in uncertainty for the wave number of about $2\pi/D$. Since the dispersion relation in each of microcrystal may be considered identical with that shown in Fig. 1, it may be considered that the Raman spectrum changes due to blurring of the wave number described above. With respect to the dispersion relation of the lattice vibration in a solid, energy lowers as the wave number increases in the optical analysis

as shown in Fig. 1. Therefore, increase in the uncertainty for the wave number q described above is observed as the increase of the scattering band intensity on the smaller Δk side by the Raman peak.

Fig. 3 shows skirt portions of primary Raman spectra for various specimens of Si including amorphous, polycrystal and single crystal. As is apparent from the figure, the side of the larger Δk than the peak in the specimens agrees with the case of the single crystal except for amorphous, which corresponds to that the energy is highest at $k = 0$ in the dispersion relation in Fig. 1. In the case of the single crystal as shown in Fig. 3, the scattering band intensity increases in the smaller Δk side as the temperature for the heat treatment lowers. This means that scattering is possible for a larger wave number region by the increase in the uncertainty of the wave number described above, which corresponds to that the scattering band intensity increases in the smaller Δk side as is apparent from the dispersion relationship. If the dispersion relationship is previously examined as described above, the crystal grain size of microcrystals can also be measured. While the explanations have been made relative to the primary Raman scattering, this can be utilized also for Raman spectrum of secondary or higher Raman spectra. However, in the secondary Raman scattering, since it may suffice that the preservation side both for the

wave number and the energy are established for the sum of the lattice vibrations concerning the scattering, the degree of change in the spectra due to the uncertainty of the wave number is usually small. Therefore, this is often not so advantageous to be used for the evaluation.

The features and the effects of the invention will become apparent with reference to the following examples.

Example 1

A method of evaluating the structure of an Si thin film by using the present invention is to be described. A monochromatic light at a wavelength of 6428 Å from a Kr ion laser was used here as an incident light for obtaining Raman spectra. Since the wavelength corresponds to an energy higher than the band gap of Si crystal, the invasion distance of the light into Si is as shallow as about 10 μm in a case of the single crystal and it is further shallower as about 1000 Å in the case of the amorphous. This is rather advantageous in the measurement for the thin film specimen. On the contrary, since an interaction distance between the light and the specimen is shortened by so much, a high sensitivity is required for the measuring instrument. The measuring device used in this example has a Kr ion laser at 100 mW of output as an light source, separates Raman scattering light from the specimen by a double mono chrometer, and conducts detection and recording by using

a light detector of a photon counting system using a photomultiplier and a recorder.

As a specimen for demonstrating the effectiveness of this evaluation method, an Si thin film of about 1 μm deposited by a heat decomposition method of silane (SiH_4) on a quartz plate was used. In this case, the structure of the Si thin film changes depending on the temperature of the substrate upon deposition. Fig. 3 shows main portions of Raman spectra for the specimens. Since Si in a crystallized state is a complete covalent bond crystal of a diamond crystal structure, primary Raman active lattice vibrations have lateral or vertical optical modes and both of them are degenerated. Therefore, the primary Raman spectrum to be observed gives only one peak. The peak appears at 525 cm^{-1} in Fig. 3. Referring to the dispersion relation in Fig. 1, this corresponds to the process of emitting lattice vibrations of the optical mode: $q \cong 0$

As is apparent from Fig. 3, upon deposition at a substrate temperature of 600 °C or higher, higher Δk sides to the primary Raman spectral peak agree with the case of the single crystal irrespective of the substrate temperature. On the other hand, in the smaller Δk sides, the scattering band intensity decreases along with increase in the substrate temperature, and approaches to the case of the single crystal. The facts can be understood in view of the dispersion relation in Fig. 1 as below. The grain size of the polycrystal decreases as

the substrate temperature lowers upon deposition of Si. Therefore, the selection rule of the Raman scattering to the wave number is moderated and vibrations for greater wave number can also be scattered. However, as apparent from the dispersion relation, since the vibration number is highest at $q = 0$, even when the selection rule of the wave number is moderated, the scattering band intensity on the larger Δk side scarcely changes. However, the scattering band intensity in the smaller Δk side increases along with lowering of the substrate temperature. As the substrate temperature further lowers to 650 °C or lower, the peak position itself changes and displaces to the side of the lower wave number. It should be considered that the dispersion relation itself has been changed. According to the experiment of electron diffraction (N. Nagashima & N. Kubota: JJA p 14 1105 (1975)), it is found that Si is amorphous at 600 °C or lower and it may be considered that the spectra in the figure correspond to the dispersion relation of amorphous Si. As described above in this example, adequacy of the crystallinity can be evaluated by measuring the Raman scattering band intensity at two different wavelengths (for example, at 525 cm^{-1} and 500 cm^{-1}) and determining the ratio therebetween.

Fig. 4 shows a relation between the average grain size of a polycrystal Si thin film measured by transmission type electron microscopic images and the Raman scattering band

intensity ratio at Δk being 525 cm^{-1} and 500 cm^{-1} determined by the measurement of the Raman spectra for the identical specimen. Further, the positions for the spectral peaks are also plotted relative to the grain size. When such a relation is once determined, the average grain size can be determined by merely measuring the Raman scattering band intensity ratio.

Further, while there is no clear definition for the amorphous and the polycrystal, assuming the state in which a blurred ring pattern appears in usual electron diffraction image as amorphous, it is known that a specimen of 30 Å in average grain size is amorphous in Fig. 4. Since the Raman peak displaces to the smaller side of Δk side corresponding to this fact, this method also has a feature capable of discriminating the amorphous and the polycrystal by measuring the peak shift.

The measuring method according to the invention can be summarized as below.

(1) A method of evaluating the structure of a material in which the crystallinity of the material is measured by taking notice of one or more of spectral bands in the Raman scattering spectrum of the material and utilizing that the half width thereof or the scattering band intensity of a skirt portion of the spectral peak increases as the crystallinity of the material is worsened.

(2) A method of evaluating the crystallinity of the material in the evaluation method (1) above, which utilizing the fact

that the scattering band intensity on the side of the lower wave number shift in the primary Raman spectral band of particularly great scattering band intensity increases due to lattice defect or other irregularities.

(3) A method of discriminating the amorphous and the crystalline state by utilizing that the Raman spectrum for the material to be evaluated in the evaluation method (2) above greatly differs between the amorphous and the crystalline state and, particularly, that the primary Raman spectrum displaces to the side of the lower wave number when it becomes amorphous.

Brief Description of the Drawings

Fig. 1 is a diagram showing the dispersion relation of lattice vibration in a crystal material, Fig. 2 is a view for explaining the primary Raman scattering process, Fig. 3 is a graph showing the change of Raman spectra to the change of substrate temperature upon preparing Si thin films by heat decomposition of silane (SiH_4), and Fig. 4 is an explanatory view for determining the average crystal grain size in Si film from Raman scattering spectra.

Fig. 1

1 vibration number

2 wave number

3 optical mode

4 acoustic mode

Fig. 2

1 incident light

2 stokes light

3 anti-stokes light

4 photon energy

Fig. 3

1 Raman scattering band intensity (optional unit)

2 substrate temperature (amorphous)

3 (amorphous + polycrystal)

4 (polycrystal)

5 (polycrystal)

6 single crystal

7 primary Raman peak

8 wave number shift

Fig. 4

1 Raman scattering band intensity ratio

2 primary Raman spectral peak Δk

3 single crystal

4 intensity ratio of single crystal

5 amorphous

6 polycrystal

7 average grain size